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(54) MANUFACTURE OF EMULSIFIER-FREE ANIONIC POLYURETHANE DISPERSIONS

(71) We, BASF AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the manufacture of emulsifier-free, anionic polyurethane dispersions from which coatings with improved properties can be produced.

The manufacture of emulsifier-free, aqueous polyurethane dispersions by introducing ionic centers into the polymer molecule, dissolving the polymer in an aqueous organic solvent and removing the organic solvent is disclosed in, for example, U.S. Patent 3,479,310 and Angewandte Chemie, 82/2 (1970), 53—90, Verlag Chemie GmbH Weinheim.

In addition, British Patent 1,339,357 discloses that in the above context polyhydroxy-compounds having a molecular weight of from 350 to 10,000 are particularly suitable as starting materials and equimolar addition products of the alkali metal salts of α -olefinic carboxylic acids with aliphatic di-primary diamines are particularly suitable for introducing the ionic centers. Dispersion may be effected in any desired manner but the preferred method is first to react the polyhydroxy-compounds of fairly high molecular weight with excess diisocyanate, in the melt, to give a prepolymer with isocyanate end groups, to take up the prepolymer in a water-miscible organic solvent which boils below 100°C and to add to this solution an aqueous solution of the diamine containing

salt groups, followed by water. The organic solvent is then distilled off.

However, coatings produced from the dispersions thus obtained still suffer from certain shortcomings which interfere with their industrial use, especially as leather coatings. Thus, whilst it is true that if aliphatic diisocyanates are used finely divided stable dispersions are obtained, the coatings obtainable therefrom are very soft and have a rubbery hand. In contrast, aromatic diisocyanates give relatively coarse dispersions which sediment readily, and the coatings produced therefrom have unsatisfactory strength and wear resistance.

The present invention seeks to provide polyurethane dispersions which do not suffer from the above disadvantages.

We have found that this object is achieved and that the above disadvantages can be eliminated if the polyurethane ionomer is synthesized from a combination of an aliphatic diisocyanate (as hereinafter defined) with an aromatic diisocyanate, either by using first the aromatic diisocyanate and then the aliphatic diisocyanate or by using both simultaneously. The synthesis of polyurethane ionomers from these isocyanate combinations is not suggested by the art, particularly as the components are known to react at very different rates, and since the products are, surprisingly, superior to the conventional products obtained from either aliphatic or aromatic diisocyanates. The new products form finely divided, stable dispersions from which hard and at the same time tough coatings having excellent strength and wear resistance can be produced.

The result of combining an aliphatic diisocyanate with an aromatic diisocyanate to

synthesize the polyurethane ionomers according to the invention is the incorporation of fairly long polar segments of aromatic diisocyanate and chain extenders into the polymer molecule. The polyurethane obtained then contains not only segments of aromatic diisocyanate, separated from one another by fairly long chains of, for example, polyesters or polyethers, and chain extenders without salt groups, but also segments of aliphatic diisocyanate and chain extenders, which do contain ionic groups. This is an essential feature of the invention. Such a segmented molecular structure obtained by combining an aliphatic diisocyanate and an aromatic diisocyanate when manufacturing the dispersions leads to an advantageous combination of properties, i.e. the dispersions are stable and finely divided, and impregnations, coatings and films obtained from the dispersions have excellent mechanical properties. The above disadvantages of the conventional products are thereby overcome.

Accordingly, the present invention relates to a process for the manufacture of an emulsifier-free, anionic, aqueous dispersion of a polyurethane prepared from

(A) a dihydroxy-compound having a molecular weight of from 500 to 5,000,

(B) a diisocyanate component,

(C) a water-soluble salt of an aliphatic aminocarboxylic or aminosulfonic acid (preferably a diaminocarboxylic or diaminosulfonic acid) with at least one hydrogen atom bonded to a nitrogen atom but preferably at least two hydrogen atoms bonded to two different nitrogen atoms, and

(D) a compound without salt groups, possessing two hydrogen atoms which are reactive toward isocyanate groups, and having a molecular weight of less than 300, as chain extenders,

by forming initially a solution or dispersion of the polyurethane in an aqueous-organic solvent mixture and then removing the organic solvent(s),

in which process the diisocyanate component B employed to form the polyurethane includes both an aromatic diisocyanate and an aliphatic diisocyanate (as hereinafter defined), the proportion of aliphatic diisocyanate in the diisocyanate component B being from 10 to 50 mole%, and in the formation of the polyurethane either the aromatic diisocyanate is employed first and the aliphatic diisocyanate thereafter, or both are employed simultaneously.

The dihydroxy-compounds (A) used may be the conventional polyesters, polyethers (with the exception of ethylene oxide homopolymers), polythioethers, polylactones, polyacetals, polycarbonates and polyester-amides with 2 terminal aliphatic hydroxyl groups. The molecular weights of these dihydroxy-compounds are usually from 500 to 5,000,

the range from 750 to 3,000 being particularly advantageous. Of course, mixtures of these dihydroxy-compounds of fairly high molecular weight may also be employed. Minor amounts of hydroxy-compounds with an average of more than two hydroxyl groups per molecule may be present, if desired. However, if they are present, they should be employed only in such proportions that the overall functionality does not exceed a mean value of 2.2. The use of dihydroxy-compounds alone is however normally preferred. The mean number of hydroxyl groups per molecule must on the other hand not be less than 2.

The term "aromatic diisocyanate" as used herein denotes a diisocyanate in which both NCO groups are attached to the same or different aromatic nuclei. The term "aliphatic diisocyanate" as used herein denotes a diisocyanate in which at least one NCO group is attached to a linear or cyclic aliphatic radical, and thus the term includes cycloaliphatic diisocyanates. The conventional aliphatic diisocyanates, e.g. 1,4-butane diisocyanate, 1,6-hexane diisocyanate, 2,2,4- and 2,4,4-trimethylhexamethylene diisocyanate, cyclohexane diisocyanate, methylcyclohexane diisocyanate, 4,4'-diisocyanatodicyclohexylmethane and isophorone diisocyanate, may be used, as may the conventional aromatic diisocyanates, e.g. xylylene diisocyanate, 4,4'-diisocyanatodiphenylmethane, 2,4- and 2,6-toluylene diisocyanate. Industrial mixtures of isomers may be used, where appropriate. Mixed aliphatic-aromatic diisocyanates (i.e. having one—NCO attached to an aromatic nucleus and the other to an aliphatic group) can also be used in place of the purely aliphatic diisocyanates in the process according to the invention. The molar ratio of the aliphatic diisocyanate to the aromatic diisocyanate in the diisocyanate component B is from 1:1 to 1:9 and preferably from 1:2 to 1:6.

Suitable water-soluble salts of aliphatic aminocarboxylic acids or aminosulfonic acids (C) are disclosed, above all, in British Patent Specification 1,339,357, but also, for example, in British Patent Specification 1,329,565. They are preferably alkali metal salts, especially sodium and potassium salts, of the adducts of a lower aliphatic di-primary diamine, e.g. ethylenediamine, with an unsaturated carboxylic acid, e.g. acrylic acid, methacrylic acid, crotonic acid or maleic acid, or alkali metal salts of lysine. In general, compounds which have at least two hydrogen atoms bonded to two different nitrogen atoms and have only one salt group in the molecule, i.e. compounds which, though they make the product dispersible, do not make it excessively hydrophilic, and which furthermore can act as chain extenders, are preferred. The alkali metal salts of the adducts

of propanesultone with an aliphatic di-
primary diamine are also very suitable. The
salts (C) are generally used in such amounts
that the total polyurethane composition con-
tains from 0.02 to 1% by weight of $-\text{CO}_3^-$
or $-\text{SO}_3^-$ groups (the weight of the cation
being left out of account).

Low molecular weight chain extenders (D)
without salt groups and having a molecular
weight of less than 300 which may be used
include the conventional glycols, eg. ethylene
glycol, propylene glycol, butane-1,3-diol and
butane-1,4-diol, hexanediol, neopentylglycol,
cyclohexanediol, 2,2-bis-(4-hydroxycyclo-
hexyl)-propane, 2,2-bis-(4-hydroxyethoxy-
phenyl)-propane, diethylene glycol and dipro-
pylene glycol, diamines, eg. ethylenediamine,
hydrazine, piperazine, isophoronediamine,
toluylenediamine, diaminodiphenylmethane,
N,N'-dimethylethylenediamine and amino-
alcohols, and under certain circumstances
also water. It is true that, formally, amino-
alcohols and primary diamines have more
than two hydrogens capable of reacting with
isocyanate groups, but in fact they behave
only as bifunctional compounds toward iso-
cyanate groups under conventional reaction
conditions, and it is this which matters.

The isocyanate groups and the hydroxyl
and amino groups capable of reacting with
isocyanate are generally employed in about
equivalent molar ratios. The ratio of the
number of isocyanate groups to the number
of total hydrogen atoms capable of reacting
with isocyanate will generally be from 0.9
to 1.2, preferably from 1.0 to 1.1.

Components A, B, C and D are generally
employed in such molar ratios that the molar
ratio of the fairly high molecular weight
hydroxy-compound (A) to the sum of the
diisocyanates (B) and to the sum of the
compound (C) containing salt groups and the
low molecular weight chain extender (D), i.e.
A:B:(C+D), is from 1:2:1 to 1:14:13.
The range from 1:4:3 to 1:10:9 is parti-
cularly advantageous. These figures apply to
the preferred case where component C is
bifunctional i.e. possesses two hydrogens
bonded to different nitrogens. For other
cases, the figures alter appropriately.

The conventional known catalysts, eg.
dibutyl-tin dilaurate, tin-II octoate or 1,4-
diazabicyclo-(2,2,2)-octane, may be used to
accelerate the reaction of the diisocyanates.

The polyurethane composition is generally
manufactured in the conventional manner
by reacting the fairly high molecular weight
polyhydroxy-compound with the diisocyan-
ates and the low molecular weight chain ex-
tender without salt groups, under atmos-
pheric or superatmospheric pressure, in the
melt or in the presence of a water-miscible,
inert organic solvent which boils below
100°C, to give a prepolymer with terminal
isocyanate groups.

The aromatic and aliphatic diisocyanates
(B) to be used according to the invention can
be reacted either as a mixture with one an-
other or successively, in the stated sequence,
with the fairly high molecular weight di-
hydroxy-compound (A) and the low mole-
cular weight chain extender (D). Because of
the different reactivity of the two diisocyan-
ates it frequently suffices to employ the
diisocyanates as a mixture with one another.
If they are reacted successively with the
hydroxy-compounds A and D, it is essential,
according to the invention, to employ the
aromatic diisocyanate first and the aliphatic
diisocyanate thereafter, to ensure that the
reaction product possesses central segments
of aromatic diisocyanate and chain extender
(D) and terminal aliphatic isocyanate groups.
If the reaction of the two diisocyanates is
carried out stepwise, it is not essential that
the aromatic diisocyanate should have re-
acted completely before the aliphatic diiso-
cyanate is added; instead, it is frequently
possible to add the aliphatic diisocyanate at
a point in time at which only a part of the
aromatic diisocyanate has reacted.

The resulting polyurethane with terminal
aliphatic isocyanate groups is dissolved in
or may be diluted, or further diluted, with
a water-miscible solvent which boils below
100°C and is inert toward isocyanate groups;
after dilution, if any, the polyurethane is
mixed, generally at from 20 to 50°C, with
a preferably aqueous solution of a salt of
an aliphatic aminocarboxylic acid or amino-
sulfonic acid of the type referred to under
C. The reaction of the salt with the isocyan-
ate groups takes place spontaneously and
results in chain lengthening if the said salt
contains more than one N—H group per
molecule. Unless the solution of the amino-
carboxylic or aminosulfonic acid salt already
provides enough water, additional water is
stirred into the solution of the resulting poly-
urethane, possessing salt-like groups as struc-
tural units, and the organic solvent is re-
moved by distillation.

This gives finely divided, stable disper-
sions which can, if required, be concentrated
by evaporation. In general, solvent-free
latices having a solids content of from 30
to 50% by weight are preferred.

Suitable low-boiling solvents are polar sol-
vents which are inert toward isocyanates,
boil below 100°C and are water-miscible,
eg. acetone, tetrahydrofuran or methyl ethyl
ketone.

The dispersions may be manufactured in
accordance with, for example, the following
general instructions: the fairly high mole-
cular weight, predominantly difunctional,
hydroxy-compound (A) is first dehydrated
at 120°C for 30 minutes under reduced
pressure from a waterpump; it is then mixed
with the chain extender free from salt groups

(D) and reacted, in the presence or absence of solvents, with a mixture of the two diisocyanates (B), or first with the aromatic diisocyanate and then with the aliphatic diisocyanate, at from 50 to 130°C, to give a prepolymer with terminal isocyanate groups. The material is then diluted with solvent (or further solvent), to give a solution of from about 30 to 50% by weight strength. A solution of the alkali metal salt of the diamino-carboxylic acid or diaminosulfonic acid in water is then added to the prepolymer solution. After completing the reaction at from 20 to 50°C, the calculated amount of additional water (if any) corresponding to the desired solids content of the dispersion to be produced is added and the solvent is distilled off under reduced pressure.

The dispersions thus obtained are fine and are stable for more than 6 months even at tropical temperatures. They can be processed by conventional methods to give films, sheets, coatings, finishes and impregnations, with a great variety of substrates. The dispersions are particularly suitable for leather coating. They have excellent adhesion to leather, are elastic, strong, tough and resistant to mechanical stress, and impart a pleasing hand.

Depending on their intended use, the polyurethane dispersions may also be combined with conventional modifiers and additives, e.g. crosslinking agents, plasticizers, pigments and fillers. They can also be blended with suitable dispersions of natural or synthetic polymers, eg. nitrocellulose.

In the Examples and Comparative Experiments, parts and percentages are by weight.

EXAMPLE 1

203 parts of a commercial polyester obtained from adipic acid, hexanediol and neopentylglycol and having an OH-number of 55 are dehydrated for 30 minutes in a stirred flask at 130°C under 20 mm Hg. The polyester is cooled and dissolved in 200 parts of acetone, and 40.5 parts of butane-1,4-diol are added. A mixture of 69.7 parts of toluylene diisocyanate (isomer ratio 2,4/2,6=80/20) and 33.6 parts of hexamethylene diisocyanate, as well as 0.02 part of dibutyl-tin dilaurate, are then added. After stirring for 3 hours at 60°C, the mixture is diluted with 300 parts of acetone and cooled to room temperature. 19.3 parts of a 40% strength aqueous solution of the equimolar addition product of ethylenediamine with sodium acrylate are then stirred into the resulting solution of the prepolymer. After 20 minutes, 500 parts of water are added dropwise and the acetone is then distilled off under reduced pressure.

A very fine, stable dispersion is obtained, which shows no tendency to sediment even

on prolonged storage. If the dispersion is dried on glass plates, clear, very glossy and very tough films are obtained, which have a tensile strength of 330 kp/cm² and an elongation at break of 720%, both measured in accordance with DIN 53,504.

COMPARATIVE EXPERIMENT 1a

Using the method described in Example 1, 203 parts of the polyester employed there are dehydrated, dissolved in acetone and mixed with 36 parts of butane-1,4-diol. The amount of the butanediol chain extender is here reduced, compared to Example 1, by the same number of moles as the amount of chain extender containing salt groups is increased. The total number of moles of chain extenders is accordingly the same in both experiments. After adding 104.4 parts of toluylene diisocyanate (80/20 isomer mixture) and 0.02 part of dibutyl-tin dilaurate, the experiment is continued as described in Example 1, except that twice the amount (15.4 g, dissolved in 23 g of water) of the chain extender containing salt groups (an adduct of ethylenediamine with sodium acrylate) is employed.

The dispersion obtained after distilling off the acetone is very coarse in spite of the salt group content being twice that of Example 1, and starts to sediment immediately. If the salt group content was lower, such sedimentation would of course be even more pronounced. The dispersion is therefore unusable for practical purposes.

COMPARATIVE EXPERIMENT 1b

Comparative Experiment 1a is repeated with an equimolar amount (100.8 parts) of hexamethylene diisocyanate in place of toluylene diisocyanate.

The prepolymer becomes insoluble in acetone after a short time, and precipitates. A dispersion cannot be obtained.

If no butane-1,4-diol is employed as the chain extender and, accordingly, only 43.8 parts of hexamethylene diisocyanate are employed instead of 100.8 parts, whilst otherwise retaining the same procedure, a fine stable dispersion is obtained, but this dispersion gives coatings which are very soft and have a rubbery hand, and are therefore unsuitable for most purposes.

COMPARATIVE EXPERIMENT 1c

241.5 parts of the polyester from Example 1 are degassed and reacted at 60°C with 36 parts of toluylene diisocyanate (TDI 80). The product is diluted with 700 parts of acetone and a mixture of 50 parts of water, 3.76 parts of ethylene-diamine, 4.26 parts of propanesultone and 19.6 parts of 10% strength aqueous sodium hydroxide solution is added. 360 parts of desalinated water are then added dropwise and the acetone

is distilled off under pressure. The dispersion obtained sediments after only a few hours.

EXAMPLE 2

401 parts of a commercial polyester obtained from adipic acid and ethylene glycol, and having a molecular weight of 2,000, are dehydrated and then diluted with 124.9 parts of neopentylglycol and 230 parts of acetone. 325 parts of 4,4'-diisocyanatodiphenylmethane and 44.5 parts of isophorone diisocyanate are then added, whilst stirring, and after the addition stirring is continued for one hour. The mixture is diluted with 900 parts of acetone and cooled to room temperature, and 38.5 parts of a 40% strength aqueous solution of the equimolar adduct of ethylenediamine with sodium acrylate are stirred in. After 30 minutes, 1,350 parts of desalinated water are slowly added dropwise and the acetone is stripped off under reduced pressure.

A very fine, stable dispersion having a solids content of about 40% is obtained. Samples coated onto glass plates dry at room temperature to give tough films which have a tensile strength of 24 N/mm² and an elongation at break of 430%, measured according to DIN 53,504, and a tear propagation resistance, measured according to DIN 53,775, of 56 kp/cm.

COMPARATIVE EXPERIMENT 2a

Example 2 is repeated under identical conditions except that instead of the isophorone diisocyanate an equimolar amount, ie. 34.85 parts, of toluylene diisocyanate (TDI 80) is employed.

The dispersion obtained begins to sediment after only a few hours and a thick sediment forms overnight. Accordingly, the dispersion produced with 2 aromatic diisocyanates is unusable for practical purposes.

EXAMPLE 3

Example 2 is repeated except that instead of the polyester 400 parts of polytetrahydrofuran of molecular weight 2,000 are employed. The water is added at 50°C and in addition 500 parts of tetrahydrofuran are also introduced.

A fine, stable dispersion is obtained, which dries at room temperature to give tough, hazy films. The films are found to have a tensile strength of 45.3 N/mm², an elongation at break of 385% and a tear propagation resistance of 66 kp/cm.

EXAMPLE 4

509 parts of a commercial polyester obtained from adipic acid, hexanediol and neopentylglycol and having a mean molecular weight of 2,000 are dehydrated, 112.6 parts of butane-1,4-diol and 230 parts of

acetone are added, and the mixture is stirred with 241.6 parts of toluylene diisocyanate (TDI 80) for 90 minutes, with the acetone boiling gently. 42.06 parts of hexamethylene diisocyanate and 0.2 part of dibutyl-tin dilaurate are then added and stirring is continued for 90 minutes. The batch is then diluted with 900 parts of acetone, and at 40°C 63.3 parts of a 32.8% strength aqueous solution of sodium lysinate are stirred in. After 20 minutes, 1,250 parts of desalinated water are slowly added dropwise, whilst stirring, and the acetone is distilled off under reduced pressure.

A fine, very stable dispersion having a solids content of 40% is obtained. Even after standing for 6 months at room temperature, no sediment has formed. Samples coated onto glass plates dry at room temperature to give clear, very glossy and very tough films which have a tensile strength of 37 N/mm², and an elongation at break of 750%.

EXAMPLE 5

100 g (0.1 mole) of a commercial polyoxypropylenediol are dehydrated, mixed with 45.06 g of butane-1,4-diol and 50 g of acetone and reacted with 99.56 g of toluene diisocyanate (TDI 80) at 55°C. After 30 minutes, 0.04 ml of dibutyl-tin dilaurate are added and 16.82 g of hexamethylene diisocyanate after one hour total reaction time, and stirring is continued for two hours. The mixture is diluted with 400 g of acetone, and 19.28 of the 40% strength aqueous solution of the adduct of ethylenediamine with sodium acrylate used in Examples 1 to 3 are added at 50°C. Then 500 ml of distilled water are added dropwise and the acetone is distilled off under reduced pressure.

A finely divided, stable dispersion is obtained which dries at room temperature to give hard and very tough films.

WHAT WE CLAIM IS:—

1. A process for the manufacture of an emulsifier-free, anionic, aqueous dispersion of a polyurethane formed from

(A) a dihydroxy-compound having a molecular weight of from 500 to 5,000,

(B) a diisocyanate component,

(C) a water-soluble salt of an aliphatic aminocarboxylic acid or aminosulfonic acid with at least one hydrogen atom bonded to a nitrogen atom, and

(D) a compound without salt groups, possessing two hydrogen atoms which are reactive towards isocyanate groups, and having a molecular weight of less than 300, as chain extender, by forming initially a solution or dispersion of the polyurethane in an aqueous-organic solvent mixture and then removing the organic solvent(s), in which process the diisocyanate component B em-

- ployed to form the polyurethane includes both an aromatic diisocyanate and an aliphatic diisocyanate (as hereinbefore defined), the proportion of aliphatic diisocyanate in the diisocyanate component B being from 10 to 50 mole%, and in the formation of the polyurethane either the aromatic diisocyanate is employed first and the aliphatic diisocyanate thereafter or both are employed simultaneously.
2. A process as claimed in claim 1, wherein the polyurethane is formed from components A—D in a molar ratio of A:B:(C+D) of from 1:2:1 to 1:14:13, component C possessing two hydrogen atoms bonded to different nitrogen atoms.
3. A process as claimed in claim 1 or 2, wherein a urethane prepolymer with isocyanate groups at both chain ends is first manufactured by reacting the components A, B and D, at from 50 to 130°C, with or without a catalyst, as a melt or in a water-miscible inert solvent which boils below 100°C and is inert towards isocyanate, the solution of the prepolymer in a water-miscible inert solvent is then reacted at from 20 to 50°C by mixing with an aqueous solution of a sufficient amount of the aminocarboxylic acid salt or aminosulfonic acid salt (component C) that the finished polyurethane, which is now in the form of a dispersion, contains from 0.02 to 1% by weight of $-\text{CO}_2^-$ or $-\text{SO}_3^-$ groups, additional water is optionally added, and the solvent is then distilled off to leave an aqueous dispersion.
4. A process as claimed in any of claims 1 to 3, wherein the component A is selected from polyesters, polyethers other than polyethylene oxide, polythioethers, polylactones, polyacetals, polycarbonates and polyesteramides.
5. A process as claimed in any of claims 1 to 3, wherein a polyester or a polyether other than polyethylene oxide is employed as component A.
6. A process as claimed in claim 4 or 5, wherein the material used as component A has a molecular weight of from 750 to 3,000.
7. A process as claimed in any of claims 1 to 6, wherein the aliphatic diisocyanate and the aromatic diisocyanate employed as component B are employed in a molar ratio of 1:2 to 1:6.
8. A process as claimed in any of claims 1 to 7, wherein a water-soluble salt of an aliphatic diaminocarboxylic acid or of a diaminosulfonic acid, with at least one hydrogen atom on each of the two nitrogen atoms, is employed as component C.
9. A process as claimed in any of claims 1 to 8, wherein a glycol, diamine, or aminoalcohol is employed as component D.
10. A process for the manufacture of an emulsifier-free, anionic, aqueous polyurethane dispersion carried out substantially as described in any of the foregoing Examples.
11. Emulsifier-free, anionic aqueous polyurethane dispersions when manufactured by a process as claimed in any of claims 1 to 10.
12. Films, sheets, coatings, finishes and impregnations when obtained by processing a dispersion as claimed in claim 11.
13. Leather which has been coated with a dispersion as claimed in claim 11 and dried to remove water.

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